



# Structural, electrochemical and theoretical study of a new chalcone derivative containing 3-thiophene rings



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## ABSTRACT

The title chalcone, 1,3-di(thiophene-3-yl)prop-2-en-1-one (C<sub>11</sub>H<sub>8</sub>OS<sub>2</sub>) is an essentially planar molecular with its terminal thiophene rings subtending an angle of 8.9°. The crystal structure consists in the  $\pi \cdots \pi$  stacking of molecules defining columns along [010], further linked along *c* by non conventional C–H $\cdots$ O bonds, thus determining broad planar arrays parallel to (100). In addition, there are weak S $\cdots$ S contacts connecting these weakly interacting 2D substructures. The experimental results obtained from single crystal X-ray diffraction data and the theoretical geometry calculated by molecular mechanics are in good agreement.

Electrochemical records reveal an anodic profile with an unsymmetrical irreversible peak at 1.77 V and a shoulder at 1.62 V vs SCE, a behavior interpretable as due to the oxidation of reactive sites present in the molecule. On the other hand, the electrochemical reduction shows a narrow peak at –1.58 V vs SCE, a fact attributable to the carbonyl group.

Finally, the values for the energy involved in the departure/arrival of electrons from border orbitals, as calculated using DFT, is compared with experimental data from cyclic voltammetry.

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## 1. Introduction

Chalcones,  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds, are a particular subclass of flavonoids [1] with a high therapeutic and preventive potential for many diseases showing antibacterial, antifungal, antitumor and anti-inflammatory properties [2–7]. In addition, chalcones have been electropolymerized for its use as organic light emitting diodes (OLED) [8–11] and they also have a broad range of applications as part of non-linear optical (NLO) [12–17], electrochemical [18,19] or fluorescent [20] materials.

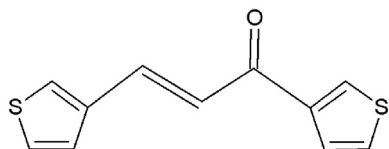
This research is propelled by the search for ligands that lead to polymetallic coordination compounds. An  $\alpha$ ,  $\beta$ -unsaturated carbonyl system, can be attacked by a nucleophilic species, resulting in a compound with different electron-donating atoms, *i.e.*, a ligand with greater tendency to coordinate specific ions. On

the other hand, these unsaturated carbonyl compounds attached to aromatic rings may result in conjugated systems, and are thus promising candidates to be provided with interesting physicochemical properties. These characteristics have led us to choose electrochemical techniques in order to investigate their electronic nature [21–25]; in this sense it is very important the work done by Morealeda et al. [26], who found a significant correlation between the halfwave potential of  $\alpha$ , $\beta$ -unsaturated carbonyl compounds, the LUMO-HOMO energies and Hammett  $\sigma/\rho$  constants.

Herein we present a thorough study (synthesis, crystal and molecular structure, spectroscopic and electrochemical characterization) of 1,3-di(thiophene-3-yl)prop-2-en-1-one, C<sub>11</sub>H<sub>8</sub>OS<sub>2</sub>, (hereinafter **3cvd**), a new functionalized chalcone containing 3-thiophene rings (Scheme 1). A density functional theory (DFT) study has also been carried out in order to predict the redox potential. Trends and correlations have been established for experimental parameters (such as ionization potential and energy of border orbitals) with theoretically calculated values.

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**Scheme 1.** Structure of 1,3-di(thiophene-3-yl)prop-2-en-1-one, **3cvd**.

## 2. Experimental

### 2.1. Synthesis and characterization

Compound **3cvd** was synthesized according to the literature [27–30], using 3-thiophenecarboxaldehyde and 3-acetylthiophene. The product was recrystallized from a methanol/water mixture and dried under vacuum at 40 °C. The FT-IR spectrum was recorded on a Shimadzu, IR-Prestige-21, using KBr pellets.

### 2.2. Electrochemical setup

Experimental setups to perform cyclic voltammetry (CV) have been described elsewhere [27–34]. In this study, the electrochemical experiments were performed in a Wavenow USB potentiostat/galvanostat (PINE research instruments, USA): a glassy carbon electrode (GCE) (Bioanalytical System, BASI) of 0.28 cm<sup>2</sup> geometric area was used as working electrode. The reference electrode was Ag/AgCl in tetraethylammonium chloride solution. The potential was adjusted with respect to the saturated calomel electrode (SCE) [35]. As auxiliary electrode a platinum coil was used, in a separated compartment from the working electrode. Before each experiment the working electrode was polished with alumina slurry (particle size 0.3 μm) on a polish microcloth and further rinsed with deionized water and acetonitrile. Anhydrous acetonitrile (Aldrich Chemical Co) was used as solvent and manipulated with syringe. The electrolyte support, tetrabutylammonium tetrafluoroborate, (TBABF<sub>4</sub>) (Aldrich Chemical Co) was dried under vacuum at 40 °C for 24 h.

The solution was gasified with argon during 15 min after each experiment, then an inert atmosphere was kept during electrochemical perturbation.

### 2.3. X-ray diffraction

Diffraction patterns were recorded with a Bruker SMART AXS CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and a semi-empirical absorption correction based on symmetry equivalent reflections was applied. A total of 35757 reflections were collected, providing a unique data set of 2940 reflections ( $R_{\text{int}} = 0.061$ ) of which 81.4% had  $I > 2\sigma(I)$ . The structure was solved by direct methods with SHELXS [36] and refined by the full-matrix least-squares based on  $F^2$  using SHELXL-2014 [37]. Structure analysis was performed with the aid of Platon software [38]. Publication material was generated using PubCif software [39] (for Tables) and XP int the SHELXTL crystallographic package [36] (for Figures).

Crystal data, data collection and structure refinement details are summarized in Table 1.

### 2.4. Computing calculations

All structures, neutral and cation species were full optimized using B3LYP/6-311 + G(d,p) level of theory. A vibrational frequency calculation is used to determine whether the structure is a minimum or saddle point on the potential energy surface and to compute the ZPE and  $\Delta G^0 \rightarrow 298 \text{ K}$  terms. Solvent effects of Acetonitrile on the thermodynamic calculations were considered by using a self-consistent reaction field (SCRF) performed using the SMD implicit solvation model [40]. The SMD solvation model uses the integral equation formalism of the polarizable continuum model (IEF-PCM) with a parametrized set of atomic radii to calculate the bulk electrostatic energy contribution. Values of free energies in Acetonitrile were calculated with standard statistical thermodynamics under reaction conditions. All computations were carried out with the Gaussian 09 suite of programs [41].

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	C <sub>11</sub> H <sub>8</sub> OS <sub>2</sub>
$M_r$	220.29
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
$a, b, c$ (Å)	22.675 (5), 4.0340 (9), 11.174 (3)
$\beta$ (°)	90.002 (4)
$V$ (Å <sup>3</sup> )	1022.1 (4)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.48
Data collection	
Diffractometer	Smart apex II, Bruker (CCD area detector)
Absorption correction	–
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	35757, 2940, 2394
$R_{\text{int}}$	0.061
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.708
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.046, 0.142, 1.03
No. of reflections	2940
No. of parameters	127
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.39, -0.38

Computer programs: SHELXL2014/6 (Sheldrick, 2014).

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